

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C09J 153/02	A1	(11) International Publication Number: WO 00/22062 (43) International Publication Date: 20 April 2000 (20.04.00)
(21) International Application Number: PCT/EP99/07759 (22) International Filing Date: 8 October 1999 (08.10.99) (30) Priority Data: 98308255.3 9 October 1998 (09.10.98) EP		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: DUPONT, Martine, Jeanne; Avenue Jean Monnet 1, B-1348 Ottignies, Louvain-La-Neuve (BE). MAYENEZ, Catherine; Avenue Jean Monnet 1, B-1348 Ottignies, Louvain-La-Neuve (BE).		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: RADIATION-CURABLE ADHESIVE		
(57) Abstract		
<p>The present invention relates to a radiation-curable adhesive comprising: (a) a block copolymer comprising at least two mono-alkenyl aromatic hydrocarbon blocks and at least one butadiene block, wherein the 1,2-vinyl content in the butadiene block is at least 25 % by weight; (b) from 100 to 300 parts by weight of a tackifying resin, per 100 parts by weight of block copolymer, wherein the tackifying resin is partially hydrogenated hydrocarbon resin, having an unsaturation index (Ui) in the range from 3 to 25 %; (c) 5 to 100 parts by weight of a partially or fully saturated oil; (d) optionally a photo-initiator; and (e) one or more stabilisers; wherein the glass transition temperature (Tg) as calculated by the Fox equation based on Differential Scanning Calorimetry is in the range from -15 °C to -5 °C. The present invention further relates to radiation-cured adhesives and to articles, in particular tapes, containing the radiation-curable or radiation cured adhesives.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		

RADIATION-CURABLE ADHESIVE

Field of the Invention

The present invention relates to adhesives, in particular radiation-curable adhesives, having a high peel adhesion and a high temperature resistance. The 5 present invention further relates to articles containing the adhesive.

Background of the Invention

Radiation-curable adhesives are well known in the art. Recently, Shell Chemicals has developed block copolymers containing styrene blocks and butadiene blocks, where the butadiene blocks have a 1,2 vinyl content of more than 25% by weight. One of such block copolymers is sold under the trade name KRATON D-KX-222, and is especially developed to be radiation curable (KRATON is a trademark).

However, the high vinyl content of KRATON D-KX222 which is necessary for fast radiation curing, in particular fast UV curing, leads to a higher tendency to gel in a hot-melt tank than standard styrene - butadiene - styrene block copolymers containing butadiene having a 1,2-vinyl content of up to 25% by weight. It was observed that gel is formed in adhesives aged for 16 hours at 160 °C. Many applications however, require a gel-free time of 24 hours at 160 °C.

As reported in "Communication from SRTCL 1-98", published by Shell Research and Technology Centre Louvain-la-Neuve in January 1998, this problem is solved by using a combination of different stabilisers. Specific examples that were mentioned are a combination of IRGANOX 1010 and IRGAFOS 168, optionally in combination with IRGANOX 3052, and a combination of SUMILIZER GS and

SUMILIZER TP-D, IRGANOX and IRGAFOS are trademarks and IRGANOX and IRGAFOS stabilisers are available commercially from Ciba-Geigy. SUMILIZER is a trademark and SUMILIZER stabilisers are commercially available from Sumitomo.

These effective stabiliser systems for retarding gelling in adhesives stored in a hot-melt tank will only be useful in a practical sense if they do not retard the gelling induced by radiation curing. As reported in the aforementioned Communication, this was not at all a problem, despite the fact that e.g. SUMILIZER GS and IRGANOX 3052 are anti-gelling agents.

The potential of these and other stabiliser combinations in adhesive compositions containing high vinyl content block copolymers, was also reported in EP-B-0243956, the contents of which are incorporated herein by reference.

Radiation curable hot melt adhesives containing block copolymers having butadiene blocks with a high 1,2-vinyl content have been described in WO 93/24547 and WO 97/29140, the contents of which are incorporated herein by reference.

WO 97/29140 discloses an adhesive composition containing 100 parts of a block copolymer, 75 parts of a fully saturated oil and 225 parts of a partially hydrogenated hydrocarbon resin (HERCULES MBG 264). The Tg was -16 °C (HERCULES MBG is a trademark).

WO 97/29140 further discloses adhesive compositions containing liquid tackifying resins rather than a partially or fully saturated oil. However, especially for hot-melt adhesive compositions, the Shear Adhesion Failure Temperature is too low for high temperature applications. Moreover, use of liquid tackifying resins increases the price of the total adhesive formulation, and the maximum curing speed is not sufficiently high.

WO 93/24547 discloses an adhesive composition containing 100 parts of a block copolymer, 15 parts of a fully saturated oil and 90 parts of a partially hydrogenated hydrocarbon resin (FORAL 85). The Tg was - 18 °C (FORAL is a trademark).

There is still a need for improved radiation-curable adhesive compositions. In particular, it would be desirable if a radiation-curable adhesive, preferably a radiation-curable hot melt adhesive, could be found that meet the requirements desirable for the most demanding tape applications, such as a high peel adhesion according to the peel adhesion 180° test (ASTM-D3330M-83), preferably combined with a high shear adhesion failure temperature (SAFT).

Such adhesives have now been found.

Summary of the Invention

Therefore, according to a first aspect, the present invention relates to a radiation-curable adhesive comprising

- (a) a block copolymer comprising at least two mono-alkenyl aromatic hydrocarbon blocks and at least one butadiene block, wherein the 1,2-vinyl content in the butadiene block is at least 25% by weight;
 - (b) from 100 to 300 parts by weight of a tackifying resin, per 100 parts by weight of block copolymer, wherein the tackifying resin is a partially hydrogenated resin, having an unsaturation index (Ui) in the range from 3 to 25%
 - (c) 5 to 100 parts by weight of a partially or fully saturated oil;
 - (d) optionally a photo-initiator; and
 - (e) one or more stabilisers;
- wherein the glass transition temperature (Tg) as calculated by the Fox equation based on Differential

Scanning Calorimetry is in the range from -15 °C to -5 °C.

According to a second aspect, the present invention relates to a radiation-cured adhesive composition obtainable by radiation curing of a radiation-curable hot melt adhesive composition as described herein.

According to a third aspect, the present invention relates to articles containing a radiation-curable hot melt adhesive composition as described herein, or a radiation-cured adhesive composition as described herein.

According to a fourth aspect, the present invention relates to a tape comprising a layer of a radiation-curable hot melt adhesive composition as described herein, or a radiation-cured adhesive composition as described herein, coated on a film.

Detailed description of the Invention

Block copolymers are well known to those skilled in the art. Block copolymers are typically prepared by anionic polymerisation. The preparation of block copolymers is well known to those skilled in the art and has been described in e.g. US patents 3,265,765; 3,231,635; 3,149,182; 3,238,173; 3,239,478; 3,431,323; Re. 27,145, and many handbooks including "Thermoplastic Elastomers, a comprehensive review" (1987), edited by N.R. Legge, G. Holden, H.E. Schroeder, Hanser publishers.

The 1,2-vinyl content in the butadiene block can be increased to more than 25% by polymerising butadiene in the presence of a modifier.

Modifiers to be suitably used for this purpose can be selected from the group consisting of ethers, amines and other Lewis bases and more in particular from the group consisting of dialkyl ethers of glycols. Most preferred modifiers are selected from dialkyl ether of ethylene glycol, containing the same of different terminal alkoxy groups and optionally bearing an alkyl substituent on the

middle ethylene radical, such as monoglyme, diglyme, diethoxy ethane, 1,2-diethoxy-propane, 1-ethoxy, 2-tert.-butoxy ethane, of which 1,2-diethoxy propane is most preferred.

5 The 1,2-vinyl content in the butadiene block is preferably in the range from 30 to 70% by weight, more preferably in the range from 35 to 65% by weight.

The mono-alkenyl aromatic monomer is typically selected from styrene, C₁-C₄ alkylstyrene and C₁-C₄ dialkylstyrene, in particular styrene, α-methylstyrene, o-methylstyrene or p-methylstyrene, 1,3-dimethylstyrene, p-tert.-butylstyrene or mixtures thereof, most preferably styrene.

15 The block copolymer preferably has a mono-alkenyl aromatic hydrocarbon content in the range of from 10 to 50% by weight, more preferably in the range of from 12 to 35% by weight.

The block copolymer may be linear or radial and typically has the structure A-B-A or (A-B)_nY, with n being an integer from 2 to 100, preferably 2 to 20, more preferably 2 to 6 and Y being the residue of a coupling agent; wherein A is a poly(mono-alkenyl aromatic hydrocarbon) block and B is a poly(butadiene) block.

20 According to a particularly preferred embodiment, the block copolymer has the general structure (AB)_pX(B¹)_q, wherein A is a poly(mono-alkenyl aromatic hydrocarbon) block and B and B¹ are the same or different poly(butadiene) blocks, wherein X is the residue of a multivalent coupling agent having a maximum of active sites (m) in the range of from 3 to 6, wherein the number average value of p is in the range from 1.5 to (m-0.5), and the number average value of q is from 0.5 to (m-1.5). It will be appreciated that if p is on average 1.5, the block copolymer is a mixture of block copolymers, in

which one component has the structure $(AB)_1X(B)_q'$ and another component has the structure $(AB)_2X(B)_q''$.

Accordingly, this mixture includes a block copolymer comprising at least two mono-alkenyl aromatic hydrocarbon blocks.

Preferably, the average sum of p and q values is less than m and the coupling efficiency is less than 95%, and more preferably more than 55%. Preferably, the sum of p and q values is more than 2.

The coupling efficiency as used herein is the coupling efficiency (in % by weight) as determined by gel permeation chromatography (GPC) of the total coupling process.

It will be appreciated by a person skilled in the art, that the sum of the p and q values is determined by the coupling efficiency (CE).

According to a particularly preferred embodiment said coupling efficiency is in the range of from 60 to 95%, more preferably from 75 to 92% and even more preferably from 80 to 91%.

The above block copolymers can suitably be incorporated in adhesive sealant and coating compositions which are radiation cured in their final form as well as in compositions which are not cured in their final form.

These block copolymers show a combination of:

- an optimum UV reactivity/melt viscosity balance, due to their high poly (conjugated diene) molecular weight and vinyl content incorporated in one radial structure.
- a distribution of composing individual molecules, some of them being particularly suited for UV sensitivity (high molecular weight) whereas smaller ones have appeared to confer high tack property before and after UV-curing.

- the mixtures of block copolymers obtained show a significantly decreased hot melt viscosity in the complete adhesive composition under usual processing temperatures.

5 Preferably, the respective number average values of p and q in the radial multiarmed block copolymers are in the range from 1.5 to m-1.5, wherein m represents the maximum functionality of the coupling agent.

10 More preferably the radial multiarmed block copolymers have been derived from trivalent or tetravalent coupling agents.

15 According to one of the preferred embodiments, a trivalent or a tetravalent coupling agent, such as trinonyl phenyl phosphite, tetrachloro silane (SiCl_4), tetramethoxy silane ($\text{Si}(\text{OMe})_4$), diethyl adipate, dimethyl adipate, and gamma-glycidoxyl-propyl-trimethoxy-silane (gamma-GPTS) is used, more preferably gamma-GPTS or trinonyl phenyl phosphite.

20 The A blocks in said block copolymers have in general a weight average molecular weight in the range of from 5,000 to 50,000 preferably from 7,000 to 25,000 and most preferably from 9,000 to 17,000. The B and B1 blocks in said block copolymers may have the same or different apparent molecular weight in the range of from 15,000 to 250,000 and preferably from 20,000 to 100,000.

25 The block copolymers of the present invention preferably have a total apparent molecular weight in the range of from 50,000 to 500,000, more preferably from 150,000 to 350,000.

30 With the term "apparent molecular weight" as used throughout the specification is meant the molecular weight of a polymer as measured with gel permeation chromatography (GPC) using polystyrene calibration standards (according to ASTM D-3536).

Tackifying resins are well known to those skilled in the art and a wide variety of different tackifying resins is available commercially. The tackifying resin to be used in the present invention is preferably a partially hydrogenated hydrocarbon resin or a rosin ester.

The partially hydrogenated tackifying resin preferably has an unsaturation index (Ui) in the range from 5 to 22%, more preferably from 7 to 20%, in particular from 7 to 17%. If a mixture of tackifying resins is used, the mixture preferably should have an unsaturation index in any one of the above ranges.

The unsaturation index is determined by ^{13}C NMR according to the procedure outlined in Canadian patent specification CA 1337218, incorporated herein by reference.

The tackifying resin typically has a softening point as determined by the Ring and Ball method (ASTM E 28) of at least 70 °C, preferably in the range of from 75 to 125 °C, more preferably 80 to 105 °C.

According to a particularly preferred embodiment, the tackifying resin is a partially hydrogenated hydrocarbon resin.

The tackifying resin is preferably present in an amount from 100 to 220 parts by weight per 100 parts by weight of block copolymer, more preferably from 150 to 200 parts by weight per 100 parts by weight of block copolymer.

The radiation-curable adhesive composition of the present invention further comprises a partially or fully saturated oil. Preferably, the partially or fully saturated oil is a naphthenic oil.

The partially or fully saturated oil is preferably present in an amount from 10 to 75, more preferably 15 to 70 parts by weight per 100 parts by weight of block copolymer.

The block copolymer, the tackifying resin and the oil are admixed such that the glass transition temperature (Tg) is at least -15 °C, preferably at least -13 °C, more preferably at least -12 °C. The glass transition 5 temperature is not more than -5 °C, preferably not more than -7 °C, more preferably not more than -8 °C, as calculated by the well-known Fox equation based on Differential Scanning Calorimetry (DSC).

$$\frac{1}{\text{Adhesive Tg}} = \frac{\text{WTPE}}{\text{TgTPE}} + \frac{\text{W resin}}{\text{Tg resin}} + \frac{\text{W oil}}{\text{TG oil}}$$

WTPE, W resin and W oil are the weight fractions of the polybutadiene block(s) of the block copolymers; tackifying resin; and oil respectively. The weight 15 fraction of WTPE is defined as weight polybutadiene block(s) (wtB) divided by [wtB + weight of resin + weight of oil].

TgTPE, Tg resin and Tg oil are the glass transition temperatures of the butadiene block(s) of the block co-polymer; the tackifying resin; and the oil respectively. 20

The total amount of block copolymer in the composition is preferably from 20 to 50% by weight, more preferably from 25 to 45% by weight, even more preferably from 27 to less than 35% by weight.

25 As indicated earlier the compositions of the present invention can be cured depending on the final end use of the compositions. Such curing is performed by exposure to high energy ionizing radiation such as electron beam radiation or by UV radiation.

30 The electron beam radiation or high energy ionizing radiation which employed to effect the cross-linking reaction can be obtained from any suitable source such as an atomic pile, an electron gun, a resonant transformer accelerator, a Van de Graaf electron accelerator, a Lineac electron accelerator, a betatron, a synchrotron, a 35

cyclotron, or the like. Radiation from these sources will produce ionizing radiation such as electrons, protons, neutrons, deuterons, gamma rays, X rays, alpha particles, and beta particles.

5 The cross-linking reaction is conveniently effected at room temperature, but it can be conducted at depressed or elevated temperatures if desired.

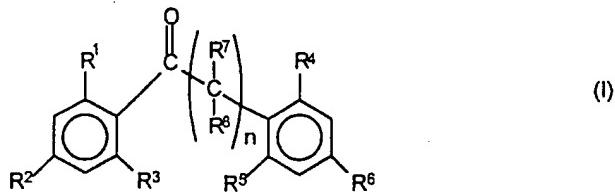
10 There is no need for strict exclusion of air during UV irradiation. Therefore it is not necessary to perform the crosslinking by UV irradiating the composition, being sandwiched between substrates such as when the composition is utilised as a tie-layer between these substrates, or in isolated equipment filled with an oxygen free inert atmosphere after evacuation.

15 It will be appreciated by a person skilled in the art that said curing by irradiation in an oxygen containing atmosphere, such as air, provides a significant cost saving.

20 The amount of irradiation required to produce a satisfactory cure depends primarily upon the type and concentration of the block copolymer employed and the unsaturation level present in the composition. Suitable dosages of electron beam irradiation are typically in the range from 0.5 to 8 Mrad, preferably from 4 Mrad to 25 8 Mrad and more preferably from 5 Mrad to 7 Mrad.

The adhesive compositions may preferably be cured by exposure to ultraviolet radiation for a period of time sufficient to effect the desired amount of cross-linking. Ordinarily, when use of ultraviolet light is contemplated, the adhesive composition will be formulated with from 0.2 to 30 parts by weight of a photo-initiator per 100 parts by the weight of the block copolymer. Any of the known photo-initiators may be used.

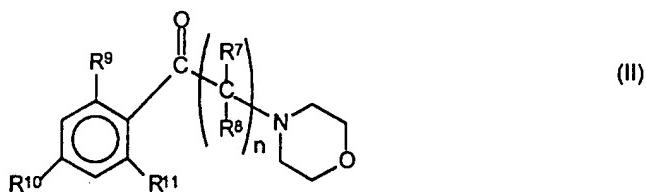
30 35 The photo-initiator, if present, is preferably selected from the group consisting of:



(1) a benzophenone of the general formula (I)

wherein R¹ to R⁶ independently represent hydrogen or an alkyl group having from 1 to 4 carbon atoms, preferably methyl, and wherein R⁷ and/or R⁸ have the same meaning as R¹ to R⁶ or represent an alkoxy group of 1 to 4 carbon atoms and wherein n has a value of 0, 1, or 2, optionally in combination with at least one tertiary amine,

5 (2) a sulphur-containing carbonyl compound, wherein the carbonyl group is directly bound to at least one aromatic ring and is preferably of the general formula II



10 wherein R⁹, R¹⁰, and R¹¹ each may represent hydrogen, alkyl of 1 to 4 carbon atoms, or an alkylthio having 1 to 4 carbon atoms, and

15 (3) and mixtures of (1) and (2).

Examples of suitable compounds of category (1) are benzo-phenone, 2,4,6-trimethylbenzophenone, 4-methyl-

benzophenone and a eutactic mixture of 2,4,6-trimethylbenzophenone and 4-methylbenzo-phenone (ESACURE TZT) and 2,2-dimethoxy-1,2-diphenylethan-1-one (IRGACURE 651) (ESACURE and IRGACURE are trademarks). These compound may
5 be employed in combination with tertiary amines, such as e.g. UVECRYL 7100 (UVECRYL is a trade mark).

Category (2) embraces compounds such as e.g. 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propanone-1, commercially available as IRGACURE 907.

10 An example of suitable mixtures (category (3)) is a mixture of 15% by weight of a mixture of 2-isopropyl-thioxanthone and 4-isopropylthioxanthone and 4-isopropyl-thioxanthone, and 85% by weight of a mixture of 2,4,6-trimethylbenzophenone and 4-methyl-benzophenone.
15 This mixture is commercially available under the trade name ESACURE X15.

In a preferred embodiment of the present invention, the photoinitiator is selected from the group consisting of (i) benzophenone, (ii) a mixture of benzophenone and a
20 tertiary amine containing a carbonyl group which is directly bonded to at least one aromatic ring, (iii) 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1 (IRGACURE 907), (iv) 2,2-dimethoxy-1,2-diphenylethan-1-one (IRGACURE 651), of which (iii) and (iv) are most
25 preferred.

It will be appreciated that the length of the exposure will be dependent on the intensity of the radiation, the amount and particular type of the ultraviolet sensitising compound employed, thickness of
30 the (adhesive) layer to be cured etc. The photoinitiators may preferably be included in an amount in the range of from 1 to 10 parts by weight per 100 parts by weight of block copolymer and more preferably in an amount in the range of from 1 to 5 parts by weight.

The UV irradiation used for cross-linking the block copolymer composition of the present invention in principle may be any UV source having an output spectrum showing one or more peaks at wavelengths between 200 and 500 nanometer (nm). Particularly suitable UV sources are Fusion bulb lamps. H and D bulb lamps (linear power 118 W/cm (300 W/inch) and 236 W/cm (600 W/inch) are particularly useful, while a combination of D bulb and H bulb lamps can also be suitably applied.

It will be appreciated that the output spectrum of any UV source has to substantially match the absorption spectrum of the photo-initiator.

The exposure to UV irradiation may be performed by any known method. A suitable method for instance is exposing a sample either in a layer obtained from a hot melt or in a layer obtained by solvent coating to UV irradiation by passing said sample at a certain speed (expressed in meters per minute, m/min) underneath the UV source. If necessary, the exposure to irradiation may be repeated one or more times, e.g. by repeatedly passing the sample underneath the UV source or by passing the sample underneath two or more lamps positioned in series, in order to accomplish sufficient curing. The lower the total irradiation dose and the higher the speed with which the sample can be passed underneath the UV source for obtaining sufficient and satisfactory curing, the better the curing ability of the said sample.

Stabilisers are typically added to the commercially available compounds in order to protect the ingredients against degradation during preparation and use of the adhesive compositions, however without interfering with the radiation curing of the polymer.

Combinations of stabilisers are often more effective due to the different mechanisms of degradation to which various polymers are subject.

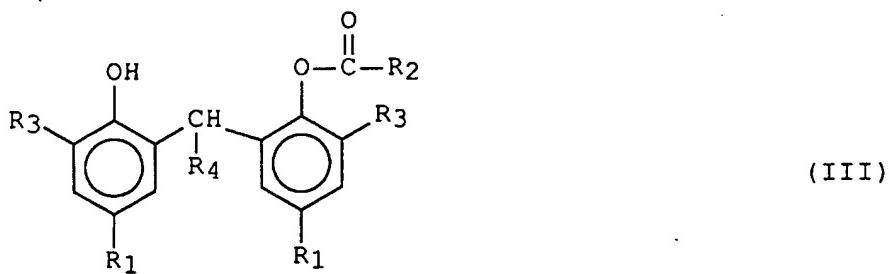
Certain hindered phenols, organo-metallic compounds, aromatic amines, aromatic phosphites and sulphur compounds are useful for this purpose.

Examples of effective types of these materials include phenolic antioxidants, thio compounds and tris-(nonylated phenyl) phosphites.

In general from 0.01 percent to 5.0 percent by weight of one or more stabilisers is included in the adhesive composition.

The radiation-curable hot melt adhesive composition of the present invention preferably contains two or more stabilisers, selected from at least two of the stabiliser categories of anti-gelling agents, primary anti-oxidants and secondary anti-oxidants. More preferably, the two or more stabilisers are selected from a combination of the following stabiliser categories of anti-gelling agents and secondary anti-oxidants; or primary anti-oxidants and secondary anti-oxidants; or a combination of all three stabiliser categories. These stabiliser categories are well known to those skilled in the art and a large variety of stabilisers in each of these categories is available commercially.

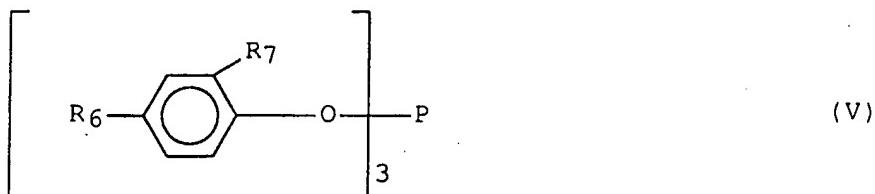
The anti-gelling agent is preferably selected from the group consisting of phenolic acrylates or methacrylates, more preferably phenolic acrylates or methacrylates represented by the general formula (III):



wherein R₁ is an alkyl group having 1 to 6 carbon atoms, R₂ is an alkenyl group having 2 to 4 carbon atoms, R₃ is

a tert-butyl, a tert-pentyl, a cyclopentyl or a cyclohexyl group, and R₄ is hydrogen or an alkyl group having 1 to 18 carbon atoms.

The secondary anti-oxidant is preferably selected from the group consisting of compounds represented by the general formula (IV) or (V):



wherein R₅ is an alkyl group having 3 to 20 carbon atoms, R₆ is an alkyl group having 3 to 20 carbon atoms or a cycloalkyl group having 5 to 20 carbon atoms, and R₇ is hydrogen, a tert-butyl, a tert-pentyl, a cyclopentyl or a cyclohexyl group, more preferably R₆ and R₇ are independently selected from a tert-butyl, a tert-pentyl, a cyclopentyl or a cyclohexyl group.

According to a particularly preferred embodiment a mixture of two secondary anti-oxidants selected from group (V) is used, the first secondary antioxidant being selected from those compounds wherein R₆ and R₇ are independently selected from a tert-butyl, a tert-pentyl, a cyclopentyl or a cyclohexyl group, such as IRGAFOS 168, and the second secondary antioxidant being selected from those compounds wherein R₆ is an alkyl group having 5 to 15 carbon atoms and R₇ is hydrogen, such as TNPP (Trisnonylphenyl phosphite). IRGAFOS 168 is a trademark for Tris(2,4-ditertiary butylphenyl) phosphite.

The primary anti-oxidant is preferably selected from the group consisting of hindered phenolic compounds.

According to one preferred embodiment three stabilisers are present, each being selected from a different stabiliser category.

Most preferably, at least two stabilisers are present, one being selected from anti-gelling agents and another stabiliser being selected from secondary anti-oxidants.

10 The invention is further illustrated by means of the following examples, without however restricting the scope of the invention to these preferred embodiments.

Examples 1-8

15 Eight radiation-curable hot melt adhesives were prepared by mixing and compounding adhesive formulations 1 to 8 shown in Table I. The mixing and compounding was carried out in a 300 g Z-blade mixer under nitrogen blanket.

20 The radiation-curable hot melt adhesives were then coated with a Chemsulant HM100 lab coater on a 36 µm polyester (PET) film. The adhesive coatings had a thickness of 40 ± 2 µm or 60 ± 2 µm.

25 The adhesive coatings were cured by UV radiation by passing the adhesive coatings at a speed of 5 m/min under a combination of two F-300 bulbs D and H from Fusion (120 W/cm). The UV rays were focused straight onto the adhesive surface in the presence of air. Peel adhesion at 180° and Shear adhesion failure temperature (SAFT) were determined before and after curing. Results are reported

30 in Table 2.

The peel adhesion at 180° was measured in accordance with ASTM-D3330M-83. The SAFT was determined as follows:

35 The SAFT test is carried out in an air circulating oven equipped with an electro-mechanical device monitoring a stepwise increase of the temperature. Inside

the oven, supports are attached to the side walls on which six aluminium racks can be placed under an angle of 2°. These racks support 6 metal (stainless steel) plates onto which the tape samples will be applied. These plates 5 rest against a narrow ridge in which 6 slots are cut; the free part of the coated film on which the weights are hung, passes along these slots.

One end of the strip is centred and stuck partially onto a stainless steel plate; the other end of the strip 10 is held so that it does not make contact with the plate but is positioned below. The strip is pressed firmly against the stainless steel plate avoiding entrapment of air bubbles. The adhered part of the strip is cut at one inch (2.5 cm) of the stainless steel edge. The surface is 15 then 2.5 cm x 2.5 cm (1 inch²). Finally, the test specimens are stored for 24 hours.

The racks with the samples are installed in the oven and weights of 500 grams are hung to the free end of the strip and clamped with "Hofmann" hose clamps.

20 These weights are initially supported by a base plate which can move up and downwards by means of a "lab jack". Just before the start of the test, the base plate is moved downwards so that the weights now hang freely above the micro or photo-electrical switches. These switches 25 are connected to a counter. The temperature in the oven is displayed on a digital thermometer.

When a strip falls, the weight falls down on the micro switch and the timer is stopped. When the time to failure is known, the temperature at which failure 30 occurred can be read off from the calculated time/temperature diagram. The SAFT value is the average of two temperatures recorded with two samples.

Comparative Example A

Another radiation-curable hot melt adhesive was 35 prepared by mixing and compounding adhesive formulation A

in the same way as in Examples 1-8. The composition of adhesive formulation A is also shown in Table I. Adhesive formulation A contained a fully hydrogenated tackifying hydrocarbon resin (REGALITE R91), having an unsaturation index (Ui) of 0.9% (REGALITE is a trademark).
5

Adhesive coatings were prepared and the coatings cured as in Examples 1-8. Peel adhesion at 180° and shear adhesion failure temperature (SAFT) were determined before and after curing. Results are reported in Table 2.

Table 1

Formulation	1	2	3	4	5	6	7	8	A
KX222	100	100	100	100	100	100	100	100	100
REGALITE S101	183		170		130		120		
MBG 264		198		183		140		130	
REGALITE R91									150
ONDINA 68	50	35	63	50	20	10	30	20	60
IRGACURE 651	3	3	3	3	3	3	3	3	3
SUMILIZER GS	1	1	1	1	1	1	1	1	1
SUMILIZER TPD	1	1	1	1	1	1	1	1	1
Tg (in °C) of formulation	-10	-10	-15	-15	-10	-10	-15	-15	-15

KX222 = KRATON D KX222, a styrenic block copolymer of idealised structure (AB)2X(B)2, wherein A is a polystyrene block and B is a butadiene block having a 1,2-vinyl content of 57% by weight. X is gamma-GPTS. The coupling efficiency is 89%.

REGALITE S101 is a partially hydrogenated hydrocarbon tackifying resin. (Ui is 8%).

MBG 264 = Hercules MBG 264, a partially hydrogenated hydrocarbon tackifying resin having an unsaturation index of 19.7%.

REGALITE R91 is a fully hydrogenated hydrocarbon tackifying resin having an unsaturation index of 0.9%.

ONDINA 68 is a saturated naphthenic oil having an unsaturation index of 2.1% (ONDINA is a trademark).

IRGACURE 651 = photo-initiator (2,2-dimethoxy-1,2-diphenylethan-1-one).

SUMILIZER GS = 2-[1-(2-Hydroxy-3, 5-di tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate.

SUMILIZER TP-D = $(RSC_2H_4COOCH_2)_4-C$ in which R is a dodecyl group.

Table 2

	Not cured		Cured			
	PA 180°, N/25mm		PA 180°, N/25mm		SAFT, °C	
	40 µm	60 µm	40 µm	60 µm	40 µm	60 µm
1	28	33	20	29	> 160	> 160
2	28	33	23	28	> 160	> 160
3	22	31	-	26	-	> 160
4	25	27	19	22	> 160	> 160
5	20	28	-	21	-	> 160
6	20	29	-	21	-	> 160
7	20	24	-	16	-	> 160
8	20	22	-	-	-	-
A	14	18	13	16	-	-

Examples 9-16

Eight radiation-curable hot melt adhesives were prepared by mixing and compounding adhesive formulations 9 to 16 shown in Table 3.

5 The radiation-curable hot melt adhesives were then coated on a polyester (PET) film. The adhesive coatings had a thickness of about 40 µm.

The adhesive coatings were cured by Electron Beam Radiation. The Electron Beam curing dose was 6 Mrad.

10 The SAFT and the peel adhesion at 180° were determined before and after curing and measured as described in Examples 1-8.

Results are reported in Table 3.

Comparative Example B

15 Another radiation-curable hot melt adhesive was prepared by mixing and compounding adhesive formulation B, coating and curing by Electron Beam Radiation as in Examples 9-16. The composition of adhesive formulation B and the results of SAFT and peel

adhesion measurements are also reported in Table 3.
Adhesive formulation B had a Tg of -16 °C.

Table 3

Formulations	9	10	11	12	B	13	14	15	16
KRATON D-KX222 C	100	100	100	100	100	100	100	100	100
REGALITE S 101	87.5	50	34.5	50	87.5	125	140.5	125	87.5
FORAL 85-E	62.5	100	115.5	100	62.5	25	9.5	25	62.5
ONDINA 68	25.5	23	28.5	40	50	52	34	34.5	37
IRGANOX 1010	1	1	1	1	1	1	1	1	1
IRGAFOS 168	2	2	2	2	2	2	2	2	2
Polymer content [%wt]	36	36.5	36	34.5	33	33	35	35	35
Tg [°C]	-9	-10	-12.5	-15	-16	-15	-9	-10	-12.5
SAFT [°C]									
cured	137	146	>150	126	123	133	>150	>150	>150
non-cured	87	87	86	81	85	86	94	93	90
Peel Adhesion [N/25 mm] 20 min									
cured	24	21	18	16	23	21	24	24	19
non-cured	28	25	21	23	19	27	24	28	22
Peel Adhesion [N/25 mm] 24 h									
cured	24	22	20	19	17	24	26	25	20
non-cured	29	27	23	23	19	27	29	28	22

FORAL 85-E is a partially hydrogenated resin ester tackifying resin, having a UI of 19.5%.

IRGANOX 1010 is tetrakis-ethylene-(3,5-di-tertiary-butyl-4-hydroxy-hydrocinnamate)methane (primary anti-
5 oxidant).

C L A I M S

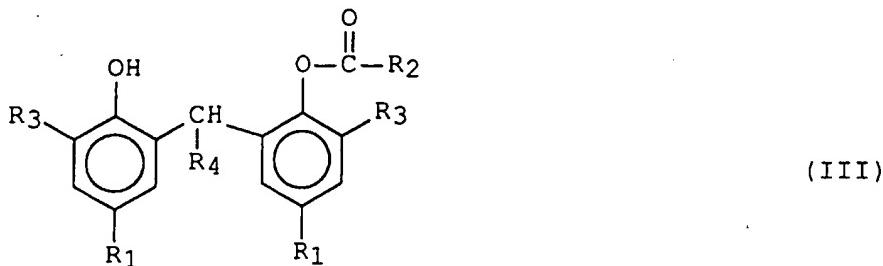
1. A radiation-curable adhesive comprising
 - (a) a block copolymer comprising at least two mono-alkenyl aromatic hydrocarbon blocks and at least one butadiene block, wherein the 1,2-vinyl content in the butadiene block is at least 25% by weight;
 - (b) from 100 to 300 parts by weight of a tackifying resin, per 100 parts by weight of block copolymer, wherein the tackifying resin is a partially hydrogenated resin, having an unsaturation index (Ui) in the range from 3 to 25%;
 - (c) 5 to 100 parts by weight of a partially or fully saturated oil;
 - (d) optionally a photo-initiator; and
 - (e) one or more stabilisers;
- 15 wherein the glass transition temperature (Tg) as calculated by the Fox equation based on Differential Scanning Calorimetry is in the range from -15 °C to -5 °C.
- 20 2. A radiation-curable adhesive as claimed in claim 1, wherein the block copolymer the 1,2-vinyl content in the butadiene block is in the range from 30 to 70% by weight.
- 25 3. A radiation-curable adhesive as claimed in claim 1 or 2, wherein the block copolymer has the general structure $(AB)_pX(B^1)_q$, wherein A is a poly(mono-alkenyl aromatic hydrocarbon) block and B and B^1 are the same or different poly(butadiene) blocks, wherein X is the residue of a multivalent coupling agent having a maximum of active sites (m) in the range of from 3 to 6, wherein the number average value of p and q is in the range from 1.5 to m.

4. A radiation-curable adhesive as claimed in claim 3, wherein the average sum of p and q values is less than m and the coupling efficiency is less than 95%.

5. A radiation-curable adhesive composition as claimed in any one of the preceding claims, wherein the tackifying resin is a partially hydrogenated resin, having an unsaturation index (Ui) in the range from 5 to 22%.

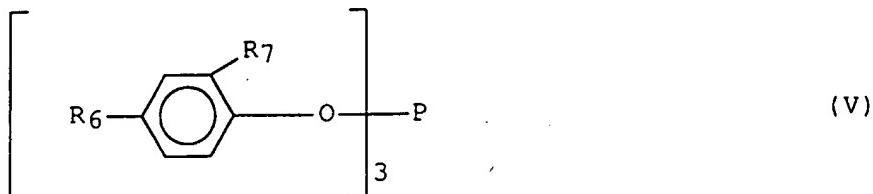
10 6. A radiation-curable adhesive composition as claimed in any one of the preceding claims, wherein two or more stabilisers are present, selected from at least two of the stabiliser categories of anti-gelling agents, primary anti-oxidants and secondary anti-oxidants.

15 7. A radiation-curable adhesive composition as claimed in claim 6, wherein the anti-gelling agent is selected from the group consisting of phenolic acrylates or methacrylates represented by the general formula (III):



wherein R₁ is an alkyl group having 1 to 6 carbon atoms, R₂ is an alkenyl group having 2 to 4 carbon atoms, R₃ is a tert-butyl, a tert-pentyl, a cyclopentyl or a cyclohexyl group, and R₄ is hydrogen or an alkyl group having 1 to 18 carbon atoms.

20 8. A radiation-curable adhesive composition as claimed in claim 6 or 7, wherein the secondary anti-oxidant is selected from the group consisting of compounds represented by the general formula (IV) or (V):



wherein R_5 is an alkyl group having 3 to 20 carbon atoms,
 R_6 is an alkyl group having 3 to 20 carbon atoms or a
cycloalkyl group having 5 to 20 carbon atoms, and R_7 is
hydrogen, a tert-butyl, a tert-pentyl, a cyclopentyl or a
cyclohexyl group.

- 5 9. A radiation-curable adhesive composition as claimed in
any one of the preceding claims 6-8, wherein the primary
anti-oxidant is selected from the group consisting of
hindered phenolic compounds.
- 10 10. A radiation-curable adhesive composition as claimed
in any one of the preceding claims 6-9, wherein at least
two stabilisers are present, one being selected from
anti-gelling agents and another stabiliser being selected
from secondary anti-oxidants.
- 15 11. A radiation-curable adhesive composition as claimed
in any one of the preceding claims, which is a hot melt
composition.
12. A radiation-cured adhesive composition obtainable by
radiation curing of a radiation-curable adhesive
- 20 20. composition as claimed in any one of the preceding
claims.
13. Articles containing a radiation-curable adhesive
composition as claimed in any one of the preceding
claims 1-11, or a radiation-cured adhesive composition as
claimed in claim 12.
- 25

14. A tape comprising a layer of a radiation-curable adhesive composition as claimed in any one of the preceding claims 1-11, or a radiation-cured adhesive composition as claimed in claim 12, coated on a film.

INTERNATIONAL SEARCH REPORT

Int. Appl. No.
PCT/EP 99/07759

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09J153/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09J C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 29140 A (SHELL INT RESEARCH) 14 August 1997 (1997-08-14) cited in the application examples table 9 claims	1-14
A	EP 0 243 956 A (ASAHI CHEMICAL IND) 4 November 1987 (1987-11-04) cited in the application examples	1-14
A	US 5 804 663 A (DUPONT MARTINE JEANNE ET AL) 8 September 1998 (1998-09-08) examples claims	1-14
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the International filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "T" document published prior to the International filing date but later than the priority date claimed

- "T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the International search

Date of mailing of the International search report

6 March 2000

16/03/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Pollio, M

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/EP 99/07759

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 24547 A (SHELL CANADA LTD ;SHELL INT RESEARCH (NL)) 9 December 1993 (1993-12-09) cited in the application examples claims	1-14
A	US 5 104 921 A (ERICKSON JAMES R ET AL) 14 April 1992 (1992-04-14) column 6, line 15 - line 40 claim 1	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intell. Jnl Application No

PCT/EP 99/07759

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9729140	A 14-08-1997	AU 707164	B 01-07-1999	
		AU 1768097	A 28-08-1997	
		BR 9707351	A 27-07-1999	
		CA 2245672	A 14-08-1997	
		CN 1210545	A 10-03-1999	
		EP 0879253	A 25-11-1998	
		HU 9900932	A 28-07-1999	
		US 5777039	A 07-07-1998	
EP 0243956	A 04-11-1987	JP 1786154	C 31-08-1993	
		JP 4074387	B 26-11-1992	
		JP 62257978	A 10-11-1987	
		JP 1815606	C 18-01-1994	
		JP 4074388	B 26-11-1992	
		JP 63027573	A 05-02-1988	
		DE 3775102	A 23-01-1992	
		KR 9003415	B 18-05-1990	
		US 4792584	A 20-12-1988	
US 5804663	A 08-09-1998	NONE		
WO 9324547	A 09-12-1993	AT 141935	T 15-09-1996	
		AU 670947	B 08-08-1996	
		AU 4322793	A 30-12-1993	
		BR 9306470	A 30-06-1998	
		CA 2137156	A 09-12-1993	
		CN 1079479	A 15-12-1993	
		DE 69304328	D 02-10-1996	
		DE 69304328	T 20-02-1997	
		EP 0643732	A 22-03-1995	
		ES 2091009	T 16-10-1996	
		FI 945671	A 01-12-1994	
		JP 7507090	T 03-08-1995	
		NO 944624	A 01-12-1994	
		US 5300582	A 05-04-1994	
US 5104921	A 14-04-1992	CA 1339778	A 24-03-1998	

THIS PAGE BLANK (USPTO)